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(54) METHOD FOR FORMING PHOTOCURED COATING

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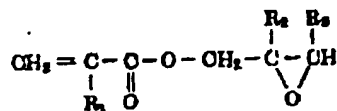
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[The amendments have been incorporated into the text of the translation.]

CLAIM

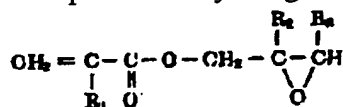
A method for forming a photocured coating, characterized by coating a substrate with a material containing a photopolymerization initiator and an acryloyl group and/or methacryloyl-group-containing drying oil-modified alkyd resin obtained by reacting a carboxy-group-containing drying oil-modified alkyd resin with an oil length of 20-80 with an unsaturated epoxy compound represented by the general formula:



(R₁, R₂ and R₃ independently represent hydrogen atoms or methyl groups) in the presence of a polymerization inhibitor, then curing the coating by activated light irradiation.

DETAILED EXPLANATION OF THE INVENTION

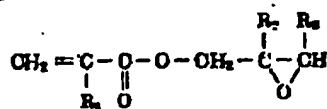
The present invention concerns a method for forming a photocured coating, characterized by coating a substrate with a material containing a photopolymerization initiator and an acryloyl group and/or methacryloyl-group-containing drying oil-modified alkyd resin obtained by reacting a carboxy-group-containing drying oil-modified alkyd resin with an oil length of 20-80 with an unsaturated epoxy compound represented by the general formula:



(R₁, R₂, and R₃ independently represent hydrogen atoms or methyl groups) in the presence of a polymerization inhibitor, then curing the coating by activated light irradiation. According to the method of the present invention, using certain coating materials described above and irradiation of activated light, even in air, coatings that are completely cured all the way to the surface are formed rapidly with good processability, chemical resistance, and water resistance.

Furthermore, it is possible to impart good printability to the coating materials of the present invention. When they are used as printing inks, photocured coatings with exceptional printing effects can be obtained on substrates by activated light irradiation, thus the method of the present invention is especially useful in printing where rapid drying is demanded.

The acryloyl group and/or methacryloyl-group-containing drying oil-modified alkyd resin (C) (hereafter referred to as resin (C)) used in the present invention can be obtained by reacting a carboxy-group-containing drying oil-modified alkyd resin (A) (hereafter referred to as resin (A)) with an oil length of 20-80 with a unsaturated epoxy compound (B) (hereafter referred to as compound (B)) represented by the general formula:



(R₁, R₂, and R₃ independently represent hydrogen atoms or methyl groups).

The carboxy-group-containing resin (A) with an oil length of 20-80 can be obtained by ordinary oil-modified alkyd resin synthesis methods, e.g., (1) alcoholysis of a drying oil and

polyol, followed by esterification with a polybasic acid; (2) reaction of a drying-oil fatty acid with a polyol and/or epoxy compound, followed by reaction with a polybasic acid; and (3) esterification of a fatty acid, polyol and/or epoxy compound, and a polybasic acid. The method should be selected according to the type of raw materials to be used and the application of the photocured coatings.

The drying oil used as the raw material for the resin (A) may be drying and semidrying oils such as tung oil, *oichishika* oil, dehydrated castor oil, linseed oil, perilla oil, safflower oil, rice bran oil, soybean oil, etc.

The drying-oil fatty acids include the fatty acids of the above drying oils, and such drying oils and fatty acids may be used alone or as mixtures thereof.

The polyols that can be used in the synthesis of the resin (A) are, e.g., diols such as ethylene glycol, propylene glycol, neopentyl glycol, etc.; triols and higher, such as glycerin, trimethylolethane, trimethylolpropane, pentaterythritol, etc.; amino alcohols such as triethanolamine, N-methyldiethanolamine, etc. The epoxy compounds that can be used in the synthesis of the resin (A) may be butyl glycidyl ether, phenyl glycidyl ether, allyl glycidyl ether, Cardura E (branched fatty acid glycidyl ester, product of Shell Co., Holland), styrene oxide, cyclohexene oxide, octylene oxide, diglycidyl sebacate, 4-vinylcyclohexene dioxide, Epikote (epoxy resin, product of Shell Co., Holland), epoxy novolak resins, etc. The above polyols and epoxy compounds may be used alone or as mixtures thereof.

The polybasic acids that can be used in the synthesis of the resin (A) may be saturated or unsaturated dibasic acids such as adipic acid, chlorendic acid, fumaric acid, isophthalic acid, succinic acid, etc.; saturated or unsaturated dibasic acid anhydrides such as chlorendic anhydride, maleic anhydride, phthalic anhydride, succinic anhydride, etc. Tribasic acids such as trimellitic acid, etc., may also be used. They may be used alone or as mixtures thereof. It is also possible to use monobasic acids such as benzoic acid, p-tert-butylbenzoic acid, crotonic acid, etc., besides the polybasic acids and drying-oil fatty acids, for a reduced average functional-group content for the prevention of gelation of the resin and resin viscosity control.

The resins (A) of the present invention are obtained by synthesis as described above. The resin (A) should have an oil length of 20-80, which is chosen within this range according to the properties required for the coatings.

Namely, for obtaining hard coatings with good solvent resistance and chemical resistance, a relatively short oil length is preferred. For obtaining coatings with better processability, a relatively long oil length is preferred. Particularly when the method of the present invention is used for the photocuring of printing inks, a relatively long oil length is needed for excellent printability.

With an oil length below 20, photocuring of the coating surface by activated light is not sufficient, while above 80, the curing speed for the coating surface and interior greatly decreases, thus is not favored.

The oil length of the resin (A) used in the present invention is determined according to the commonly accepted definition. Namely, assuming, in the resin (A), a fatty acid reacts with an equivalent polyol amount (average value if two or more polyols are used) to form fatty acid ester, the wt% in the fatty acid ester resin (A) is given.

As described above, the resin (A) can be obtained by an ordinary alkyd resin preparation process, while carrying out the reaction in an inert gas atmosphere such as dry nitrogen, helium, or carbon dioxide is preferred for the prevention of oxidative polymerization of the drying oil at the reaction temperature.

While the resin (A) preparation can be done without a solvent, the reaction may proceed more smoothly by the so-called solvent method using solvents that are inert with respect to reactants, such as toluene, xylene, etc. The reaction progress can be monitored by the acid-value measurement at certain time intervals. For the subsequent addition reaction of the carboxy group in the resin (A) and epoxy group of the epoxy compound (B), the acid value of the resin (A) used in the present invention should be in the range of 20-300.

The compound (B), a component of the resin (C) used in the present invention, may be glycidyl acrylate, glycidyl methacrylate, β -methylglycidyl acrylate, β -methylglycidyl methacrylate, etc. The ratio of the resin (A) and the compound (B) should be that needed to produce the ratio of the carboxy group in the resin (A) to the epoxy group in the compound (B) of 1:0.5 to 1:2.0, preferably 1:0.8 to 1:1.2.

The ratio of the compound (B) added to the resin (C) should be 10-40 wt%. In the reaction of the resin (A) and the compound (B), it is necessary to suppress the polymerization reaction of the ethylenically unsaturated double bond of the compound (B) as much as possible, thus it is essential to add polymerization inhibitors in the reaction system. Examples of such polymerization inhibitors include p-benzoquinone, hydroquinone, hydroquinone monomethyl ether, p-tert-butylcatechol, mono-tert-butylhydroquinone, pyrogallol, etc. Their usage amount is 0.005-1.0 wt% with respect to the compound (B). According to our experiments, with the polymerization inhibitors in the above range, even when residual polymerization inhibitors are not removed after the resin preparation, the curing speed is not adversely affected in the curing of coatings by activated light irradiation. The reaction progress can be monitored by acid-value measurement of the resin at a certain time interval. The resin (C) should have an acid value of 0-200.

While the resins (C) can be prepared without using solvents, the reaction can also be carried out in the presence of organic solvents free of active groups that are reactive to the resin

(A) and the compound (B) or ethylenically unsaturated monomers. The organic solvents may be methyl isobutyl ketone, butyl acetate, dioxane, ethylene glycol monomethyl ether acetate, toluene, xylene, kerosene, etc. The ethylenically unsaturated monomers may be styrene, ethyl acrylate, n-butyl acrylate, methyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, etc. Such solvents may be used alone or as mixtures thereof. Their amount should be less than 50 wt% with respect to the resin (C). However, when ethylenically unsaturated monomers are used for the reaction solvents, it is necessary that the ethylenically unsaturated monomers be treated with 0.005-1.0 wt% of polymerization initiators in advance. The solvents used may be removed upon completion of resination if needed, and the ethylenically unsaturated monomers may remain and be used as coating components. While the reaction between the resin (A) and the compound (B) proceeds smoothly even without a catalyst, in some cases, conventional catalysts such as 2-methylimidazole, benzyltrimethylammonium chloride, etc., can be used in an amount of 0.01-3.0 wt% with respect to the compound (B). The reaction may be carried out in air, while the reaction in an inert atmosphere is desirable for prevention of the oxidative polymerization of the drying oils in the resin (A). The reaction temperature should be selected in such a way that a polymerization reaction of the ethylenically unsaturated double bond in the reaction system is not promoted, in 70-150°C.

In the present invention, it is essential to use the resin (C) together with photopolymerization initiators. Any photopolymerization initiator that is stimulated by activated light irradiation, easily causing a photopolymerization reaction, can be used. Examples include acyloins such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, decyl bromide, α -methylbenzoin, etc.; carbonyl compounds such as 2-methylantraquinone, cyclohexanone, 9-fluorenone, etc.; diketones such as benzil, diacetyl, etc.; organic sulfides such as diphenyl monosulfide, diphenyl disulfide, decyl phenyl sulfide, tetramethylthiuram monosulfide, etc.; phenones such as acetophenone, benzophenone, phenyl 2-thienyl ketone, p,p'-tetramethyldiaminobenzophenone, etc.; sulfonyl halides such as p-toluenesulfonyl chloride, 1-naphthalenesulfonyl chloride, 2-naphthalenesulfonyl chloride, 1,3-benzenedisulfonyl chloride, 2,4-dinitrobenzenesulfonyl chloride, p-acetamidobenzenesulfonyl chloride, etc.; halogenated hydrocarbons such as carbon tetrachloride, carbon tetrabromide, hexabromoethane, iodoform, 1,1,2,2-tetrabromoethane, etc.; dyes such as eosine, thionine, fluorescein, riboflavin, 3,6-diaminoacridine, etc. These photopolymerization initiators may be used alone or mixtures thereof, in an amount of 0.1-40 wt% with respect to the resin (C). With the photopolymerization initiator used in an amount below 0.1 wt%, the photopolymerization reaction would be too slow to be practical, while above 40 wt%, no additional benefit with respect to the curing speed would be realized, not to mention it being uneconomical.

In the present invention, in addition to the resin (C) and photopolymerization initiator, if needed, organic solvents, ethylenically unsaturated monomers, polymeric compounds, free-radical generating compounds, plasticizers, fillers, pigments, dyes, and other additives may be used to obtain coating-forming materials such as coating materials, inks, etc. The overall resin (C) content in the coating forming materials should be above 30%.

The coating-forming materials are coated on a substrate and irradiated with activated light to obtain photocured coatings with rapid curing, while the irradiation may be carried out in an inert gas atmosphere if needed.

For the activated light used for curing the coating films, light with a wavelength of 2000-5000 Å is effective, from light sources such as a carbon arc lamp, mercury vapor lamp, UV fluorescence lamp, tungsten lamp, xenon lamp, argon lamp, photographic lamp, sun, etc.

In the curing of coating films in the present invention, the use of heat together with the activated light irradiation may improve the curing speed and cured-film performance.

The photocured coating-film formation process of the present invention can be used in coating or printing on glass, plastics, paper, metals, stone, wood, etc.

Next, the present invention is explained in detail with examples. However, the present invention is not limited to such examples. Parts and % are based on weight, unless stated otherwise. The viscosity is the Gardner value, and the acid value is the number of mg of potassium hydroxide reacting with 1 g of resin.

APPLICATION EXAMPLE 1

In a 4-necked flask fitted with a thermometer, stirrer, nitrogen blow inlet, and exhaust opening, 60 parts of Epikote 1001 (an epoxy resin, product of Shell Chemical Co.) were heated to melt under a nitrogen gas blow to 120°C under stirring, treated with a mixture of 40 parts of dehydrated castor oil and 0.2 part of lithium hydroxide, further heated to 180°C over a period of 1 h, kept at that temperature for 1 h, heated to 230°C over a period of 3 h, and stirred at that temperature for 2 h to obtain a transparent resin that is semi-solid at room temperature and has an acid value of about 0. The content was allowed to cool to 150°C, stirred with 42 parts of phthalic anhydride at the same temperature for 3 h to reach an acid value of 110 to obtain a dehydrated castor oil-modified alkyd resin that is a white solid at room temperature and has an oil length of 42. A ball-containing condenser was fitted in the exhaust opening of the flask, followed by the addition of 30 parts of methyl isobutyl ketone, 0.15 part of hydroquinone, and 0.2 part of 2-methylimidazole, cooling to 110°C, dropwise addition of 50 parts of β -methylglycidyl methacrylate (premixed with 100 ppm of hydroquinone methyl ether) over a period of 2 h at the same temperature, and stirring at the same temperature for 4 h to reach an acid value of about 10 to obtain a methacryloyl group-containing dehydrated castor oil-modified

alkyd resin solution. The reaction mixture was cooled to 60°C, treated with a mixture of 30 parts of methyl methacrylate (containing 50 ppm of hydroquinone), 30 parts of butyl acrylate (containing 50 ppm of hydroquinone monomethyl ether), and 30 parts of trimethylolpropane triacrylate (containing 50 ppm of hydroquinone monomethyl ether) and cooled with sufficient stirring to obtain a methacryloyl group-containing dehydrated castor oil-modified alkyd resin varnish with a viscosity of 20 P at 25°C.

100 parts of this varnish were mixed with 5 parts of benzoin methyl ether, 5 parts of benzophenone, 2.0 parts of a dimethyl phthalate solution containing 60% of methyl ethyl ketone peroxide, 0.5 part of cobalt naphthenate solution (metal content 6%), and 3.0 parts of dibutyl phthalate, and kneaded in an ordinary 3-roll mill to obtain a clear coating material, which was then evenly coated to about 50 g/m² on a pattern-paper-laminated plywood using a hand roll, and immediately irradiated for 5 sec with a 2 kW high-pressure mercury lamp (tube length 60 cm) in air at room temperature at a distance of 5 cm to obtain a beautiful decorative plywood with complete curing of the coating and a high surface hardness.

APPLICATION EXAMPLE 2

In a 4-necked flask fitted with a thermometer, stirrer, nitrogen-gas blow inlet, and water separator, 30 parts of dehydrated castor oil fatty acid, 18 parts of trimethylolpropane, 5 parts of triethanolamine, 47 parts of phthalic anhydride, and 2.0 parts of xylene were heated and stirred in a stream of nitrogen gas to reach 190°C after 1 h 30 min with heating at a constant rate. At this point, a dehydration reaction started. The heating was continued with the separation of water formed in the reaction from refluxing xylene in the water separator. The temperature reached 230°C after about 3 h. Stirring was continued at this temperature for 4 h to reach an acid value of about 100 to obtain a dehydrated castor oil-modified alkyd resin with an oil length of 34. The content in the flask was cooled to 120°C, treated with 20 parts of methyl isobutyl ketone and 0.1 part of hydroquinone to 110°C, treated dropwise with 36 parts of glycidyl methacrylate (containing 100 ppm of hydroquinone monomethyl ether) over a period of 2 h at the same temperature, and further stirred at the same temperature for 3 h to reach an acid value of 5.0 to obtain a methacryloyl group-containing dehydrated castor oil-modified alkyd resin varnish with a viscosity of 10 P at 25°C.

100 parts of this varnish were mixed with 5 parts of benzoin methyl ether, 0.1 part of rare earth octate (metal content 12%), 0.01 part of cobalt octate (metal content 12%), and 1.0 part of white petrolatum, then kneaded in an ordinary 3-roll mill to obtain a glossy varnish for metals.

A tinplate precoated and baked with a white coating based mainly on a styrenated alkyd resin was roll-coated to a thickness of about 15 g/m² with the above varnish, heated in a 180°C atmosphere for 1 min, then immediately irradiated in air with activated light from a 2 kW high-

pressure mercury lamp (product of Phillips Co., Holland) at a distance of 5 cm. The coating was completely cured in 3 sec to obtain a beautiful coating with a high surface hardness and excellent processability and adhesion.

APPLICATION EXAMPLE 3

In a 4-necked flask fitted with a thermometer, stirrer, nitrogen gas inlet, and exhaust opening, a mixture of 70 parts of tung oil, 7.0 parts of trimethylolpropane, and 0.1 part of lithium hydroxide was stirred and heated at a constant heating rate in a nitrogen gas blow to 230°C over a period of 1 h 30 min, stirred at the same temperature for 15 min, immediately cooled to 150°C, treated with 23 parts of phthalic anhydride, further cooled to 120°C, and stirred for 3 h to reach an acid value of 80 to obtain a tung oil-modified alkyd resin with a viscosity of 45 P at 25°C and oil length of 71. A solution of 0.1 part of p-benzoquinone in a mixture of 2 parts of methyl isobutyl ketone and 12 parts of trimethylolpropane trimethacrylate (containing 100 ppm of hydroquinone monomethyl ether) was then added, cooled to 90°C, treated at the same temperature with 22 parts of glycidyl acrylate (containing 100 ppm of hydroquinone monomethyl ether) in a dropwise manner over a period of 2 h, and stirred at 90°C for 3 h to reach an acid value of 8 to obtain an acryloyl group-containing tung oil-modified alkyd resin varnish with a viscosity of 80 P at 25°C. In a 3-roll mill, 70 parts of this varnish, 25 parts of Brilliant Carmine 6 B, 12 parts of benzoin methyl ether, 30 parts of a solution obtained by heating Halon 80 (ketone resin, product of Honshu Chemical Industries Co., Ltd.) and tung oil in a 1:1 ratio, and 3 parts of tridecyl alcohol were sufficiently kneaded to obtain a planographic ink.

This ink was used for printing 5000 sheets of Kamisaki Topcoat paper at a rate of 6000 sheets/h in a Rolando Faborit [transliteration] RF 01 type monochromatic machine (Faber and Schreifier [transliteration] Co., West Germany), displaying an excellent printability.

A similarly good printability was also observed with 5052H aluminum plates (thickness of 0.17 mm, product of Showa Aluminum Can Co.) in place of the Kamisaki Topcoat. Immediately after printing, the print was irradiated with activated light from two 60-cm-long 2 kW high-pressure mercury lamps at a distance of 5 cm. The ink dried in 2 sec to form a coated film with excellent friction resistance.

APPLICATION EXAMPLE 4

Using the procedure of Application Example 3, 25 parts each of phthalocyanine blue, benzidine yellow, and carbon black were used in place of 25 parts of the Brilliant Carmine 6B to obtain planographic inks (A), (B), and (C), respectively, showing excellent printability under activated light irradiation as in Application Example 3. The inks dried in the time shown in the table below to form friction-resistant coating films.

Ink	Pigment	Drying time (sec)
(A)	Phthalocyanine blue	2.3
(B)	Benzidine yellow	1.8
(C)	Carbon black	2.5

APPLICATION EXAMPLE 5

In a 4-necked flask fitted with a thermometer, stirrer, nitrogen-gas blow inlet, and ball-filled condenser, 70 parts of tung oil, 7.6 parts of pentaerythritol, and 0.1 part of litharge were stirred and heated at a constant heating rate in a nitrogen gas stream to reach 240°C after 1 h 30 min, stirred at the same temperature for 10 min, immediately cooled to 150°C, treated with 22.4 parts of succinic anhydride, cooled to 120°C, and stirred at that temperature for 3 h to reach an acid value 125 to obtain a tung oil-modified alkyd resin with an oil length of 70. Next, 0.07 part of p-benzoquinone was dissolved in the resin, heated to 110°C, treated with 35 parts of glycidyl methacrylate over a period of 2 h, and stirred at 110°C for 3 h to reach an acid value of 12 to obtain an acryloyl group-containing tung oil-modified alkyd resin with a viscosity of 60 P at 25°C. A planographic ink was obtained by kneading 65 parts of this resin, 20 parts of benzoin yellow, 10 parts of β -naphthalenesulfonyl chloride, 5 parts of benzoin ethyl ether, 10 parts of Special Solvent C (product of Nippon Sekiyu Co.), 2.0 parts of polyethylene compound (a dispersion of polyethylene in a light oil, product of Dainippon Ink Kagaku Kogyo Co.), and 3.0 parts of an organic bentonite in an ordinary 3-roll mill.

Under the printing conditions of Application Example 3, this ink was used for printing on Jet Manila carton paper (product of Daishowa Seishi Co.), displaying a good printability. The print was immediately irradiated with activated light similarly as in Application Example 3. The ink film dried in 1.5 sec and showed no strike-through when stored in a stack for 24 h.

APPLICATION EXAMPLE 6

In a 4-necked flask fitted with a thermometer, stirrer, nitrogen gas inlet, and water separator, a mixture of 55 parts of linseed oil fatty acid, 18 parts of trimethylolpropane, and 2 parts of xylene was stirred and heated at a constant heating rate in a nitrogen gas stream to reach 180°C after 1 h 30 min. At this point, dehydration started. The heating was continued with the separation of water from the refluxing xylene in the water separator, reaching 230°C after 3 h. The reaction mixture was further stirred at the same temperature for 1 h to reach an acid value of about zero, cooled to 160°C, treated with 30 parts of phthalic anhydride, heated again to 220°C, stirred at this temperature for 2 h and freed from xylene to obtain a linseed oil-modified alkyd resin with an acid value of 115 and oil length of 62, which was then cooled to 110°C, treated with 0.25 part of hydroquinone, treated at the same temperature with 60 parts of glycidyl

methacrylate over a period of 1 h, and further stirred at the same temperature for 2 h to reach an acid value of about zero to obtain a methacryloyl group-containing linseed oil-modified alkyd resin with a viscosity of about 50 P at 25°C.

An overprint varnish was obtained by kneading 90 parts of this resin and 10 parts of pentaerythritol tetrakis(β -mercaptopropionate) in a 3-roll mill.

This overprint varnish was used for solid printing on the Kamisaki Topcoat paper of Application Example 3 under the conditions used in Application Example 3, displaying an excellent printability. When irradiated with activated light under the same conditions as Application Example 3, drying occurred in 1.7 sec, with a high luster and film strength, suitable for overprint varnish.

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